



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Optical Properties Of Silicon Nanoparticles In The Presence Of Water

D. Prendergast, J.C. Grossman, A.J. Williamson,  
J. Fattebert, G. Galli

March 22, 2004

APS March Meeting  
Montreal, Canada  
April 22, 2004 through April 26, 2004

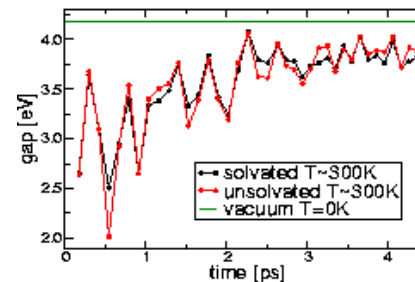
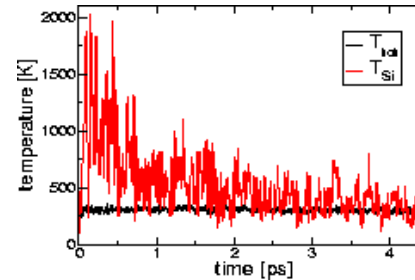
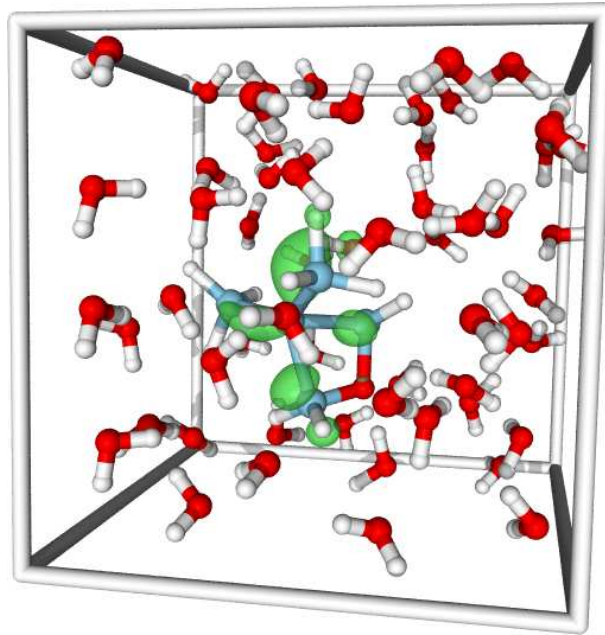
## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

# Optical properties of silicon nanoparticles in the presence of water

---



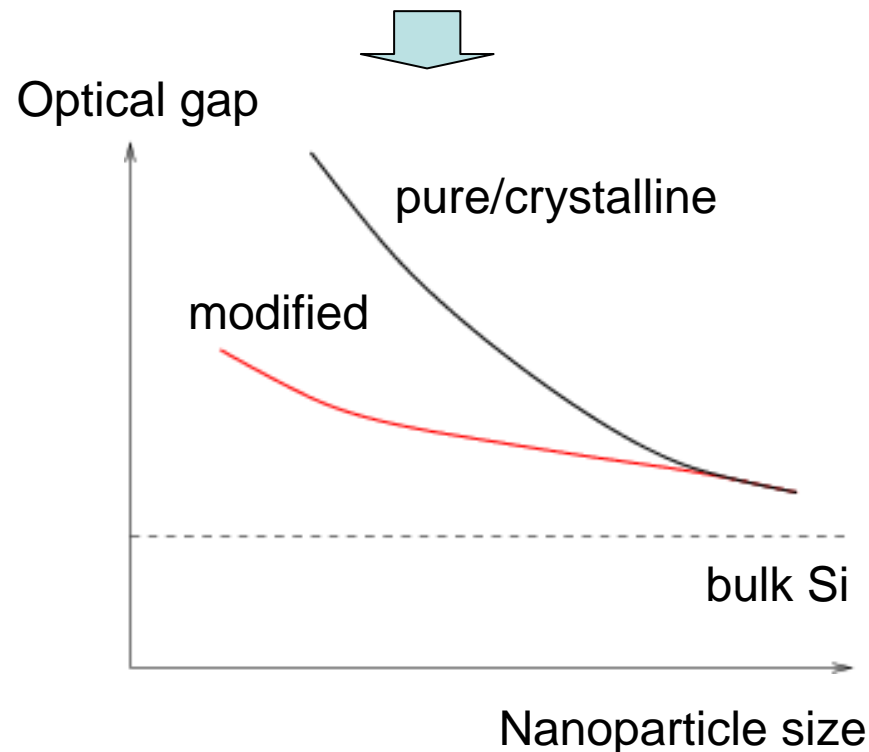
David Prendergast, Jeffrey C. Grossman, Andrew J. Williamson,  
Jean-Luc Fattebert and Giulia Galli

*Lawrence Livermore National Laboratory*

# Optical Properties of Si nanoparticles in vacuo

In summary...

A. Puzder et al, *Phys Rev Lett* **88**, 097401 (2002)  
A. Puzder et al, *J Chem Phys* **117**, 6721 (2002)  
A. Puzder et al, *Phys Rev Lett* **91**, 157405 (2003)  
E. Draeger et al, *J Chem Phys* (submitted)



Optical gaps of Si nanoparticles display quantum confinement

Various “modifications” cause decrease in optical gap – absorption red shift

- Surface chemistry: Si=O
- Complete surface hydroxylation
- Surface relaxation
- Noncrystalline core

Surface Chemistry and Strain

What about solvation?

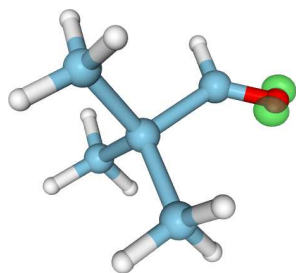
# Optical impact of solvents

---

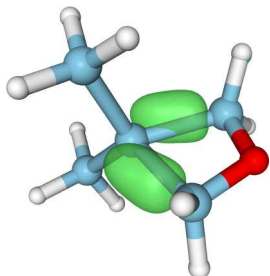
- 1) Chemical reactivity/dissociativity – alters molecular composition and structure
- 2) Finite temperature – induces molecular strain and alters electronic structure
- 3) Dielectric screening impact on absorption –
  - red shift in nonpolar solvents, e.g. benzene
  - blue shift in polar solvents, e.g. water

# Chemical stability of Si clusters in H<sub>2</sub>O

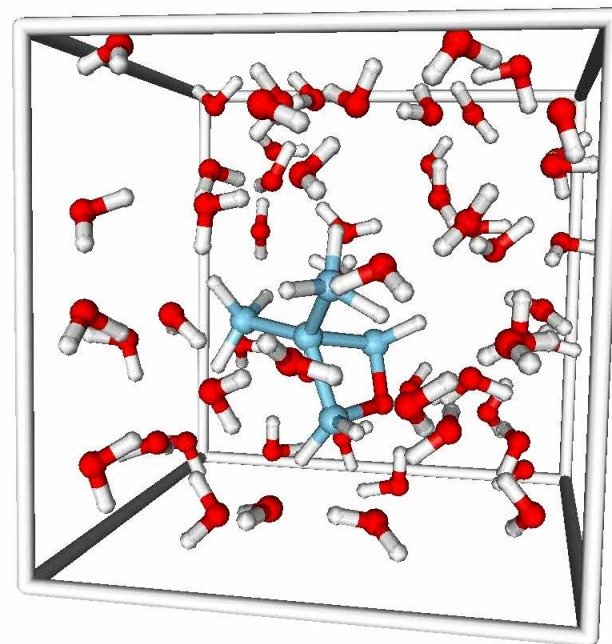
Si<sub>5</sub>H<sub>10</sub>O (I)



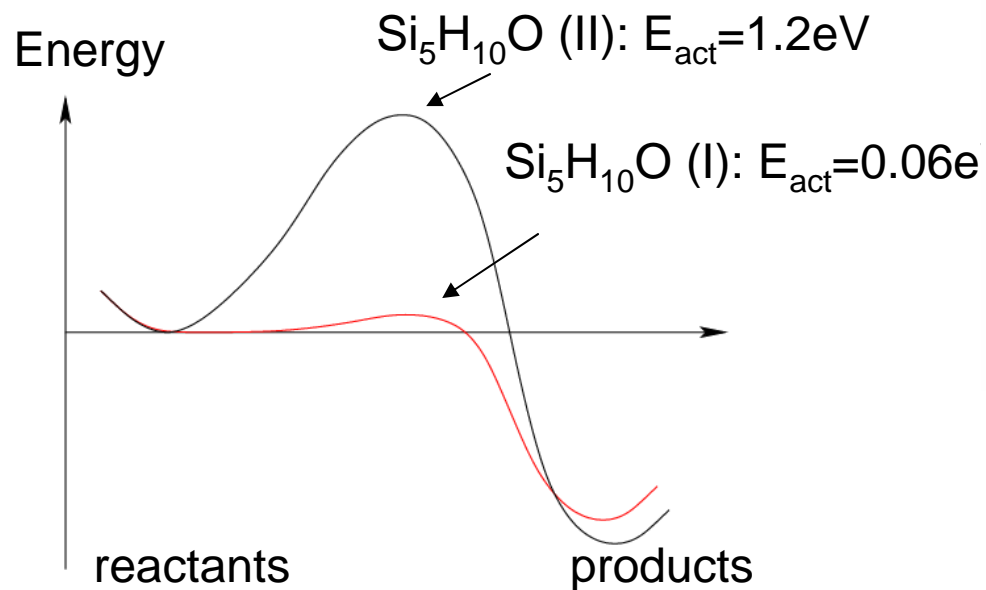
Si<sub>5</sub>H<sub>10</sub>O (I)



Complete solvation at 300K



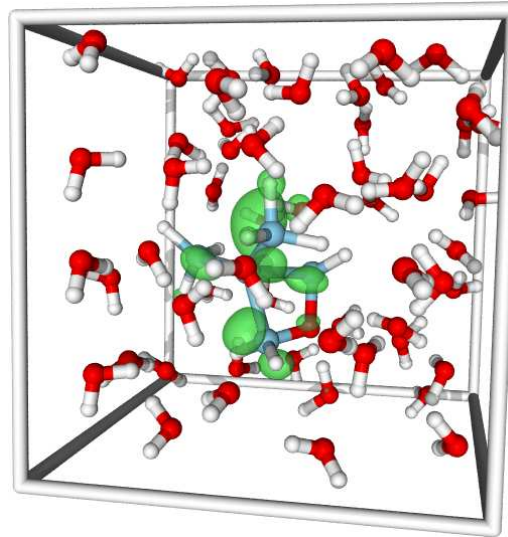
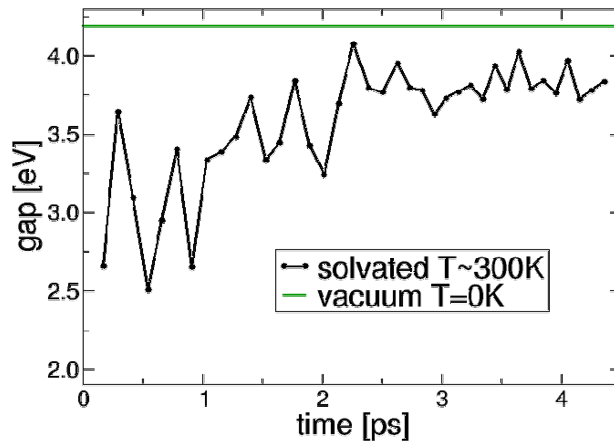
Reactivity in water vapour



# Absorption gap of Si cluster at 300K

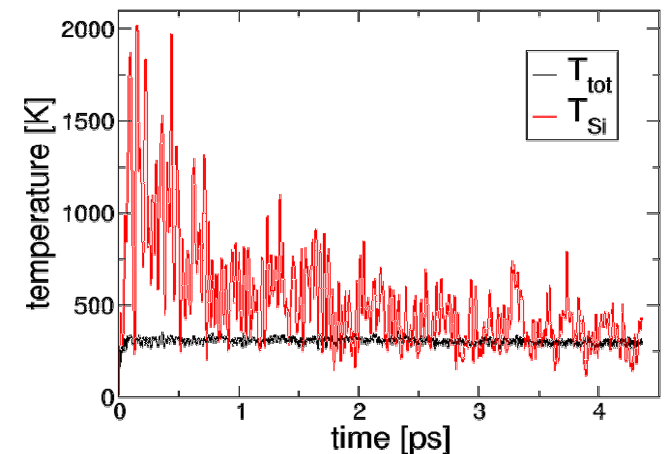
*Ab initio* MD simulation:  
 $\text{Si}_5\text{H}_{10}\text{O}$  (II) + 57  $\text{H}_2\text{O}$   
300K for 4.5ps

Absorption gap fluctuates  
wildly within 1.5 eV range



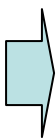
States involved in  
optical transitions  
localized on Si cluster

Fluctuations in gap  
directly correlated with  
Si cluster temperature



# Polar solvents and absorption blue shifts

Polar solvents composed of molecules with strong dipole moments



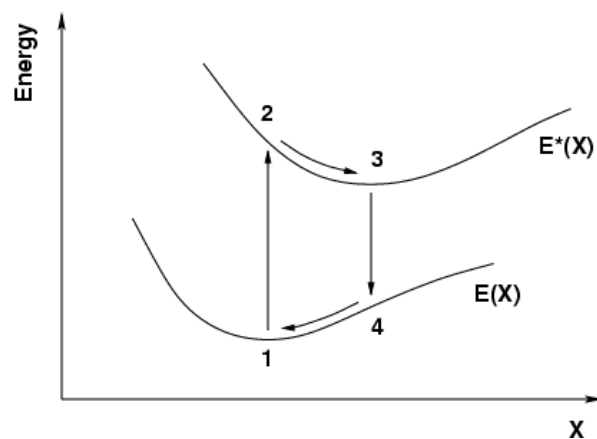
Screening requires time for solvent molecules to reorient



Liquid water –  
Debye relaxation  $\sim 1$  ps

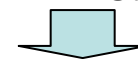
1) Ground state solute in **equilibrium** with dipole field of solvent

2) Excited state solute surrounded by frozen **ground state oriented** dipole field



Absorption and Emission process

Nonequilibrium excited state shifted higher in energy



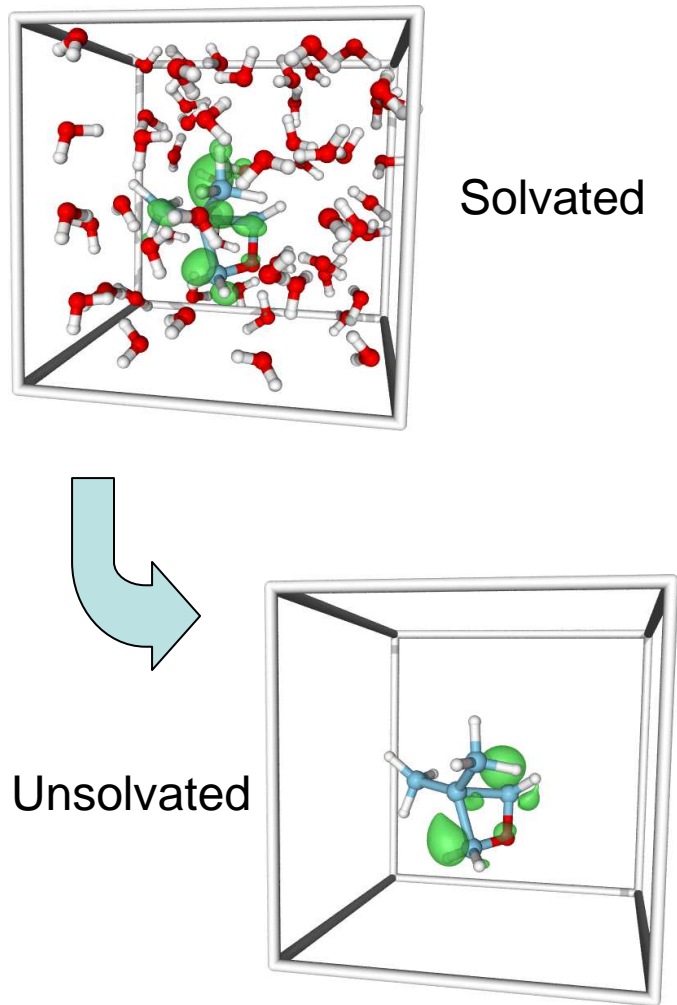
More energy required to make optical transition



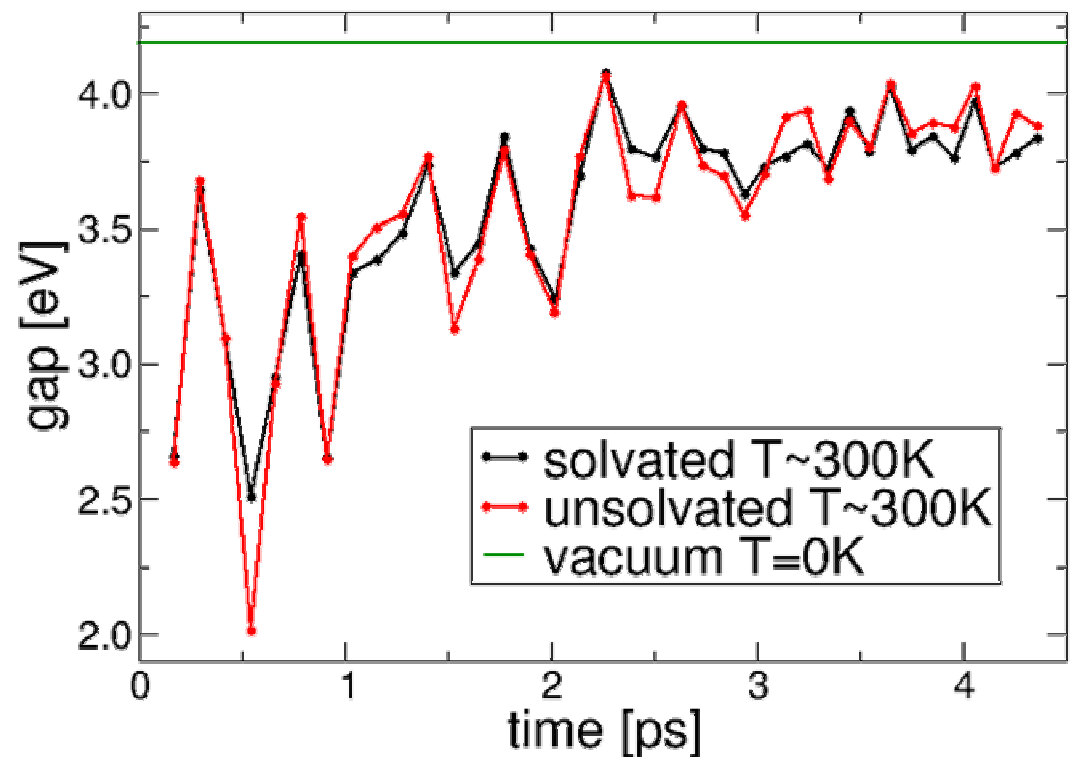
Blue shift in absorption



# No H<sub>2</sub>O screening impact for Si cluster



Removing water does not alter trend  
in absorption gap



Thermal strain provides dominant impact

# Conclusions

---

- Reactivity excludes Si=O from **red shift** in H<sub>2</sub>O
- Thermal strain in solvated Si<sub>5</sub>H<sub>10</sub>O at 300K
- Strain induced **0.7eV** red shift in absorption
- Screening impact of H<sub>2</sub>O **negligible** at 300K

*This work was performed under the auspices of the U.S. Department of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48*